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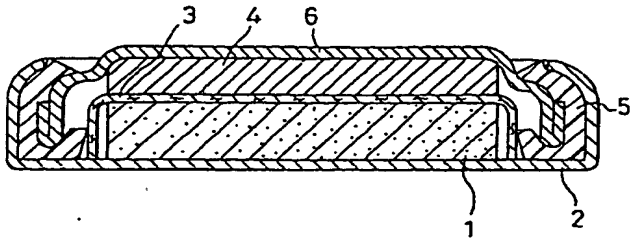
(54) Non-aqueous electrolyte secondary battery

(57) The present invention provides a non-aqueous electrolyte secondary battery having an anode active material with a high capacity and excellent cycle characteristics. The active material comprises a salt generated reacting a metal or a semi-metal and a compound selected from the group consisting of oxo-acids, thiocyanic acid, cyanogen, and cyanic acid, wherein each said oxo-acid comprises an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium, salts of said oxo-acids of phosphorus and boron being restricted to hydrogenphosphates and hydrogenborates.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

The present invention relates to an improvement in anodes of non-aqueous electrolyte secondary batteries.

Non-aqueous electrolyte secondary batteries including lithium or a lithium compound for the anode are expected to have a high voltage and high energy density, and therefore, they are extensively studied.

Known cathode active materials for the non-aqueous electrolyte secondary batteries are oxides and chalcogens of transition metals, such as $LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$, V_2O_5, Cr_2O_5, MnO_2, TiS_2, MoS_2 and the like. These compounds have a layered or tunneled crystal structure to allow lithium ions to freely intercalate and deintercalate. The use of metallic lithium for the anode active material has intensively been examined. Such use, however, has a drawback; lithium dendrite occurring on the surface of metallic lithium in the course of charging results in lowering the charge-discharge efficiency and may come into contact with the cathode to cause an inner short circuit.

In order to solve this problem, the potentials for application of lithium alloys, such as lithium-aluminum, which can depress the growth of lithium dendrite and absorb and desorb lithium, for the anode have been studied. However, when lithium alloys are used for the anode, repeated charge and discharge causes pulverization of the alloys, posing a problem of poor cycle life characteristics.

There are proposals for solving this problem by inhibiting pulverization of the alloys by including additional elements in the lithium-aluminum alloy (for example, Japanese Laid-Open Patent Publication Sho 62-119856 and Hei 4-109562), although the improvement is not sufficient. Lithium ion batteries recently developed have anodes composed of carbon material that reversibly intercalates and deintercalates lithium and has excellent cycle characteristics and safety though having a smaller capacity than those of the anode active materials mentioned above.

With a view to enhancing the capacity, a number of studies have proposed application of oxides for the anode; for example, crystalline oxides, such as SnO and SnO_2 (Japanese Laid-Open Patent Publication Hei 7-122274 and Hei 7-235293) and amorphous oxides, such as $SnSiO_3$, $SnSi_{1-x}P_xO_3$ (Japanese Laid-Open Patent Publication Hei 7-288123). These oxides, however, do not sufficiently improve the characteristics.

SUMMARY OF THE INVENTION

The object of the present invention is thus to provide an anode for non-aqueous electrolyte secondary batteries having excellent charge-discharge cycle characteristics.

The present invention provides an anode that absorbs lithium in the course of charging not to cause dendrite and has a large electric capacity and an excellent cycle life.

The present invention is directed to a non-aqueous electrolyte secondary battery comprising a cathode capable of being charged and discharged, a non-aqueous electrolyte, and an anode capable of being charged and discharged, the anode having an active material that comprises a salt of a metal or a semi-metal and a compound selected from the group consisting of an oxo-acid, thiocyanic acid, cyanogen, and cyanic acid, wherein the oxo-acid is one of an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium.

It is preferable that the metal or the semi-metal constituting the metal salt or the semi-metal salt is at least one selected from the group consisting of Al, Sn, Si, Pb, Cd, Bi, In, Zn, Mg, Ge, Ga, Ca, Ba, Ir, Sb, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Nb. Especially preferable are Sn, Pb, In, and Bi.

The present invention gives a non-aqueous electrolyte secondary battery that is free from a short circuit due to dendrite and has a high energy density, an excellent cycle life, and a high reliability.

While the novel features of the invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

Fig. 1 is a vertical sectional view schematically illustrating a test cell used for evaluating the electrode characteristics of active materials in accordance with the present invention.

Fig. 2 is a vertical sectional view schematically illustrating a cylindrical battery including an anode in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the anode of the present invention comprises a metal salt or a semi-metal salt of a specific

acid or cyanogen.

In the following description, salts of a divalent metal M^{II} are given as examples. Salts of nitrogen oxo-acids include nitrates $M^{II}(NO_3)_2$ and nitrites $M^{II}(NO_2)_2$.

Salts of sulfur oxo-acids include sulfates $M^{II}SO_4$, sulfites $M^{II}SO_3$, disulfates $M^{II}S_2O_7$, peroxomonosulfates $M^{II}SO_5$, peroxodisulfates $M^{II}S_2O_8$, thiosulfates $M^{II}S_2O_3$, disulfites $M^{II}S_2O_5$, thiosulfites $M^{II}S_2O_2$, hydrogensulfates such as $M^{II}(HSO_4)_2$, thionates such as dithionates $M^{II}S_2O_6$ and dithionites $M^{II}S_2O_4$, sulfoxylates such as $M^{II}SO_2$, and hydrogen-containing acid salts.

Preferable salts of phosphorus oxo-acids include hydrogenphosphates such as $M^{II}HPO_4$ and $M^{II}(H_2PO_4)_2$, phosphinates $M^{II}(PH_2O_2)_2$, and phosphonates $M^{II}PHO_3$.

Salts of carbon oxo-acids include carbonates $M^{II}CO_3$ and hydrogencarbonates $M^{II}(HCO_3)_2$.

Preferable salts of boron oxo-acids include hydrogenborates such as $M^{II}(H_2BO_3)_2$ and $M^{II}HBO_3$.

Salts of selenium oxo-acids include selenates $M^{II}SeO_4$, selenites $M^{II}SeO_3$, $M^{II}SeO_5$, hydrogenselenates $M^{II}(HSeO_4)_2$, and hydrogenselenites $M^{II}(HSeO_3)_2$.

Salts of tellurium oxo-acids include tellurates such as $M^{II}{}_3TeO_6$ and $M^{II}TeO_4$, and hydrogentellurates such as $M^{II}{}_5(H_5TeO_6)_2$, $M^{II}{}_2H_2TeO_6$, $M^{II}{}_3(H_3TeO_6)_2$, and $M^{II}H_4TeO_6$.

Available thiocyanates include $M^{II}(SCN)_2$, while available cyanides and cyanates include $M^{II}(CN)_2$ and $M^{II}(ONC)_2$.

The metal salt and the semi-metal salt of the present invention are, however, not restricted to the above chemical compositions.

Among the above salts, sulfates, hydrogensulfates, carbonates, hydrogenborates, and hydrogenphosphates are preferable for the improvement in cycle characteristics.

The following gives salts of oxo-acids of transition elements W, Mo, Ti, Zr, Nb, Ta, Mn, and V as examples. In the following formulae, M^{III} represents a trivalent metal or semi-metal.

Available tungstates include $M^{II}WO_4$, $M^{II}WO_3$, $M^{III}WO_6$. Available molybdates include $M^{II}MoO_4$ and $M^{III}Mo_4O_6$. Available titanates include $M^{II}TiO_3$, $M^{II}TiO_4$, $(M^{III})_2TiO_5$, and $M^{II}Ti_3O_7$.

Available zirconates include $M^{II}ZrO_3$ and $M^{II}ZrO_4$. Available chromates include $M^{III}CrO_3$, $M^{II}CrO_4$, $M^{II}Cr_2O_4$, and $(M^{III})_2CrO_6$. Available niobates include $M^{III}NbO_4$, $M^{II}Nb_2O_6$, and $(M^{III})_2Nb_2O_7$.

Available tantalates include $M^{III}TaO_4$ and $(M^{II})_2Ta_2O_7$. Available manganates include $M^{II}MnO_3$, $(M^{III})_2MnO_4$, and $(M^{III})_2MnO_6$. Available vanadates include $M^{III}VO_4$, $(M^{III})_2VO_5$, and $M^{II}V_2O_6$.

Preferable are chromates, tungstates, molybdates, vanadates, manganates, and tantalates, and especially preferable are chromates, tungstates, and molybdates for the improvement in cycle characteristics.

The metal salt and the semi-metal salt of the present invention are, however, not restricted to the above chemical compositions.

The present inventors have made an intensive study on the availability of various metal salts and semi-metal salts as the negative electrode material. It was found that such compounds can serve as the negative electrode materials with a high capacity and exceptional cycle life characteristics that have a crystal structure in which the metal or semi-metal is surrounded by a) the salts including oxygen and any one of nitrogen, sulfur, phosphorus, carbon, boron, selenium, and tellurium, such as salts of oxo-acids of nitrogen, sulfur, phosphorus, carbon, boron, selenium and tellurium or by the salts further including hydrogen such as hydrogen-containing oxo-acids; b) cyanides containing nitrogen and carbon; c) cyanates containing nitrogen, carbon and oxygen; or d) thiocyanates containing nitrogen, carbon and sulfur and in which those salts are bonded to the metal or semi-metal by ionic force.

The present inventors also discovered that such compounds can also serve as the negative electrode materials with a high capacity and superb cycle life characteristics that have a crystal structure in which the metal or semi-metal is surrounded by the salts of oxo-acid of a transition element including oxygen and any one of tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese and vanadium, that is, tungstates, molybdates, titanates, zirconates, chromates, niobates, tantalates, manganates and vanadates.

The prior art metal oxides have the greater tendency of covalent bonding and tougher skeletons than those of the metal salts and semi-metal salts in accordance with the present invention. While the prior art metal oxides are presumed to be relatively brittle under the conditions of expansion and contraction accompanied by intercalation and deintercalation of a large amount of lithium, however, the metal salts and semi-metal salts of the present invention are expected to be relatively tough under the conditions of expansion and contraction accompanied by intercalation and deintercalation of a large amount of lithium. It is also found that the existence of hydrogen in the salts of oxo-acids further improves the cycle characteristics, although the details have not yet been elucidated.

The chemical compositions of the metal salts and the semi-metal salts discussed above represent only examples of divalent or trivalent metals and semi-metals. Chemical compositions of metal salts and semi-metal salts of different valences should be apparent to the skilled in the art. For example, selenates can be expressed by the following general formulae as the metal salts and semi-metal salts of the valence m:

$M_2(SeO_4)_m$, $M_2(SeO_3)_m$, $M_2(SeO_5)_m$, $M(HseO_4)_m$, and $M(HSeO_3)_m$.

Some examples in accordance with the present invention are given below, although the anode material of the

present invention is not restricted to the chemical compositions discussed in these examples.

Example 1

Test cells shown in Fig. 1 were manufactured and tested for evaluation of the electrode characteristics of various metal and semi-metal nitrates and nitrites specified in Tables 1 and 2 and used as the anode active material.

Referring to Fig. 1, numeral 1 designates a test electrode composed of a molded mixture containing an active material. The test electrode 1 is arranged on the substantial center of a battery casing 2. A separator 3 of a micro-porous polypropylene film was placed on the test electrode 1. After injection of an electrolyte solution, the opening of the battery casing 2 is sealed with a sealing plate 6 having a counter electrode 4 composed of a metallic lithium disc of 17.5 mm in diameter on the inner surface thereof and a polypropylene gasket 5 on the circumference thereof. This completes a test cell.

The mixture included 6 g of an active material powder, 3g of graphite powder as a conductive agent, and 1 g of polyethylene powder as a binding agent. The test electrode 1 was obtained by press molding 0.1 g of the mixture to a disc of 17.5 mm in diameter. The electrolyte used was prepared by dissalving lithium perchlorate ($LiClO_4$) at a concentration of 1 mol/l in a 1:1 mixed solution (volume ratio) of ethylene carbonate and dimethoxyethane.

At a constant electric current of 2 mA, the test cell was subjected to cathode polarization (which corresponds to charging in case that the active material-containing electrode is considered as the anode) until the electrode potential became 0 V with respect to the lithium counter electrode. The test cell was then subjected to anode polarization (which corresponds to discharging) until the electrode potential became 1.5 V woth respect to the counter electrode. After the repeated cathode polarization and anode polarization, and the electrode characteristics were evaluated.

For the purpose of comparison, electrodes were manufactured in the above manner using the known compounds shown in Table 3, that is, crystalline oxides WO_2, Fe_2O_3, SnO, and PbO, sulfides SnS and PbS, and amorphous metal oxides $SnSiO_3$ and $SnSi_{0.8}P_{0.2}O_{3.1}$, and test cells were assembled and tested under the same conditions for evaluation of the electrode characteristics.

Tables 1 through 3 show the discharge capacities per one gram of the active material in the first cycle.

The measurement proved that all the test cells of Example 1 were capable of being charged and discharged. After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 1.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes including the active materials of Example 1 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium. The electrodes of Example 1 have higher capacities than those of the comparative examples.

Cylindrical batteries shown in Fig. 2 were manufactured and tested for evaluation of the cycle characteristics of the batteries using various metal and semi-metal nitrates and nitrites of Example 1.

Each battery was manufactured in the following manner.

A cathode active material $LiMn_{1.8}Co_{0.2}O_4$ was prepared by mixing Li_2CO_3, Mn_3O_4, and $CoCO_3$ at a predetermined molar ratio, heating the mixture at 900 °C, and classifying the mixture to or below 100 meshes.

A paste was prepared by mixing 100 g of the cathode active material, 10 g of carbon powder as a conductive agent, and 8 g (as the resin) of aqueous dispersion of polyethylene tetrafluoride as a binding agent, and pure water. The paste was applied onto a titanium core member, dried, and rolled out to a cathode plate.

An anode plate was manufactured by mixing a metal or semi-metal nitrate or nitrite as an active material, graphite powder as a conductive agent, and Teflon powder as a binding agent at the weight ratio of 60 : 30 : 10, adding a petroleum solvent to the mixture to yield a paste, applying the paste onto a copper core member, and drying it at 100 °C. A micro-porous polypropylene film was used as a separator.

A cathode plate 11 with a cathode lead 14 which is composed of the same material as that of the core member and attached to the cathode plate 11 by spot welding, an anode plate 12 with an anode lead 15 welded thereto, and a separator 13 having a greater width than those of these electrode plates 11 and 12 were wound in spirals to constitute an electrode group. Polypropylene insulating plates 16 and 17 were placed on the top and bottom of the electrode group, and the assembly was inserted into a battery casing 18. After formation of a step on the upper portion of the battery casing 18 and injection of the same non-aqueous electrolyte as that of the above-mentioned test cell, the battery casing 18 was sealed with a sealing plate 19 having an anode terminal 20. This completes a battery.

The batteries constructed as above were subjected to a charge-discharge cycle test at a temperature of 30 °C and a charge-discharge current of 1 mA/cm^2 in a charge-discharge voltage range of 4.3 V to 2.6 V. A rate of the discharge capacity at the 100-th cycle to the discharge capacity at the second cycle (hereinafter referred to as capacity maintenance rate) was measured.

Anode plates were prepared and test batteries were assembled in the above manner for the comparative examples. The cycle characteristics of the comparative examples were also evaluated under the same conditions.

Tables 1 through 3 show the results of evaluation.

Table 1

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al(NO_3)_3$	284	75
$Al(NO_2)_3$	326	73
$Sn(NO_3)_4$	346	86
$Sn(NO_2)_4$	389	84
$Sn(NO_3)_2$	485	84
$Sn(NO_2)_2$	510	82
$Si(NO_3)_4$	390	83
$Si(NO_2)_4$	435	84
$Pb(NO_3)_2$	356	83
$Pb(NO_2)_2$	394	82
$Cd(NO_3)_2$	320	78
$Cd(NO_2)_2$	336	77
$Bi(NO_3)_3$	298	78
$Bi(NO_2)_3$	324	75
$In(NO_3)_3$	346	78
$In(NO_2)_3$	375	75
$Zn(NO_3)_2$	289	75
$Zn(NO_2)_2$	326	79
$Ga(NO_3)_3$	335	75
$Ga(NO_2)_3$	362	72
$Gc(NO_3)_4$	367	74
$Ge(NO_2)_4$	400	72
$Mg(NO_3)_2$	296	81
$Mg(NO_2)_2$	334	79
$Sb(NO_3)_3$	425	75
$Sb(NO_2)_3$	433	73
$Ti(NO_3)_4$	275	80
$V(NO_3)_2$	255	84
$Cr(NO_2)_3$	285	82
$Mn(NO_3)_2$	263	83
$Fe(NO_3)_2$	274	81
$Co(NO_3)_2$	269	80
$Ni(NO_3)_2$	271	80
$Cu(NO_3)_2$	265	78
$Mo(NO_3)_2$	222	77
$W(NO_3)_4$	215	80
$Nb(NO_3)_3$	220	79
$Ca(NO_3)_2$	286	79
$Ba(NO_3)_2$	275	80
$Ir(NO_3)_3$	266	81
$Sr(NO_3)_2$	286	79

Table 2

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ba_{0.33}Sn_{0.67}(NO_3)_2$	425	86
$Ca_{0.33}Sn_{0.67}(NO_3)_2$	433	85
$Sr_{0.33}Sn_{0.67}(NO_3)_2$	443	85
$Mg_{0.33}Sn_{0.67}(NO_3)_2$	435	85
$Mn_{0.22}Sn_{0.78}(NO_3)_2$	410	86
$Fe_{0.12}Sn_{0.88}(NO_3)_2$	451	85
$Co_{0.18}Sn_{0.82}(NO_3)_2$	444	87
$Cu_{0.18}Sn_{0.82}(NO_3)_2$	435	86
$Ti_{0.12}Sn_{0.82}(NO_3)_2$	436	85
$Zn_{0.12}Sn_{0.88}(NO_3)_2$	442	87
$Cr_{0.12}Sn_{0.82}(NO_3)_2$	440	86
$V_{0.12}Sn_{0.82}(NO_3)_2$	421	87
$Ba_{0.33}Sn_{0.67}(NO_3)_2$	312	85
$Ca_{0.33}Pb_{0.67}(NO_3)_2$	319	87
$Sr_{0.33}Pb_{0.67}(NO_3)_2$	329	87
$Mg_{0.33}Pb_{0.67}(NO_3)_2$	326	85
$Mn_{0.22}Pb_{0.78}(NO_3)_2$	333	84
$Fe_{0.12}Pb_{0.88}(NO_3)_2$	329	86
$Co_{0.18}Pb_{0.82}(NO_3)_2$	326	85
$Cu_{0.18}Pb_{0.82}(NO_3)_2$	319	87
$Ti_{0.12}Pb_{0.82}(NO_3)_2$	314	81
$Zn_{0.12}Pb_{0.88}(NO_3)_2$	329	83
$Cr_{0.12}Pb_{0.82}(NO_3)_2$	320	84
$W_{0.09}Pb_{0.82}(NO_3)_2$	301	87
$Fe_{0.18}In_{0.88}(NO_3)_3$	324	82
$Co_{0.27}In_{0.82}(NO_3)_3$	315	83
$Cu_{0.27}In_{0.82}(NO_3)_3$	310	84
$Ti_{0.27}Bi_{0.82}(NO_3)_3$	275	80
$Zn_{0.27}Bi_{0.88}(NO_3)_3$	284	79

Table 3

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
WO_2	190	9

Table 3 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Fe_2O_3	185	10
SnO	522	5
$SnSiO_3$	453	20
PbO	453	2
SnS	498	6
PbS	436	3
$SnSi_{0.8}P_{0.2}O_{3.1}$	406	25

The batteries using the metal or semi-metal nitrate or nitrite of Example 1 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 2

Test cells discussed in Example 1 were manufactured and tested under the same conditions as those of Example 1 for evaluation of the electrode characteristics of various metal and semi-metal carbonates and hydrogencarbonates specified in Tables 4 and 5 and used as the anode active material. Tables 4 and 5 show the discharge capacities of the test cells in the first cycle.

The measurement proved that all the test cells of Example 2 were capable of being charged and discharged.

After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 2.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes comprising the active materials of Example 2 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium.

Cylindrical batteries discussed in Example 1 were manufactured and tested under the same conditions of those of Example 1 for evaluation of the cycle characteristics of the batteries using various metal and semi-metal carbonates and hydrogencarbonates of Example 2. Tables 4 and 5 show the capacity maintenance rates at the 100-th cycle.

Table 4

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(CO_3)_3$	342	75
$Al(HCO_3)_3$	306	86
$Sn(CO_3)_2$	493	86
$SnCO_3$	534	82
$Sn(HCO_3)_4$	424	92
$Sn(HCO_3)_2$	490	90
$Si(CO_3)_2$	378	81
$Si(HCO_3)_4$	365	89
$PbCO_3$	441	82
$Pb(HCO_3)_2$	402	84
$CdCO_3$	397	75
$Cd(HCO_3)_2$	365	85
$Bi_2(CO_3)_3$	369	73
$Bi(HCO_3)_3$	305	78
$In_2(CO_3)_3$	461	76
$In(HCO_3)_3$	386	85
$ZnCO_3$	298	72
$Zn(HCO_3)_2$	268	82
$Ga_2(CO_3)_3$	334	73
$Sb(HCO_3)_3$	315	75
$Ga(HCO_3)_3$	312	79
$Ge(CO_3)_2$	365	75
$Ge(HCO_3)_4$	335	83
$MgCO_3$	304	79
$Mg(HCO_3)_2$	292	85
$Ti_2(CO_3)_3$	298	75
$MnCO_3$	263	86

Table 4-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
VCO_3	198	86
$Cr_2(CO_3)_3$	263	82
$FeCO_3$	246	84
$CoCO_3$	259	83
$NiCO_3$	264	81
$CuCO_3$	253	82
$MoCO_3$	221	82
$BaCO_3$	256	80
$CaCO_3$	263	75
$W(CO_3)_2$	215	75
$Ir_2(CO_3)_3$	321	73
$Sb_2(CO_3)_3$	365	78
$Nb(CO_3)_5$	187	80
$SrCO_3$	273	75

Table 5

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ba_{0.2}Sn_{0.8}CO_3$	498	84
$Ca_{0.2}Sn_{0.8}CO_3$	485	85
$Sr_{0.2}Sn_{0.8}CO_3$	495	85
$Mg_{0.2}Sn_{0.8}CO_3$	500	86
$Mn_{0.2}Sn_{0.8}CO_3$	482	85
$Fe_{0.2}Sn_{0.8}CO_3$	479	87
$Co_{0.2}Sn_{0.8}CO_3$	486	86
$Cu_{0.2}Sn_{0.8}CO_3$	493	85
$Ti_{0.2}Sn_{0.7}CO_3$	475	84
$Zn_{0.2}Sn_{0.8}CO_3$	482	85
$Cr_{0.2}Sn_{0.7}CO_3$	473	85
$Mo_{0.2}Sn_{0.8}CO_3$	459	86
$Ba_{0.2}Pb_{0.8}CO_3$	421	83
$Ca_{0.2}Pb_{0.8}CO_3$	416	85
$Sr_{0.2}Pb_{0.8}CO_3$	416	85
$Mg_{0.2}Pb_{0.8}CO_3$	422	84
$Mn_{0.2}Pb_{0.8}CO_3$	418	87
$Fe_{0.2}Pb_{0.8}CO_3$	409	86
$Co_{0.2}Pb_{0.8}CO_3$	417	85
$Cu_{0.2}Pb_{0.8}CO_3$	415	84
$Ti_{0.2}Pb_{0.7}CO_3$	398	85

Table 5-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Zn_{0.2}Pb_{0.8}CO_3$	405	86
$Cr_{0.2}Pb_{0.7}CO_3$	403	85
$Mo_{0.2}Pb_{0.8}CO_3$	398	87
$(Fe_{0.3}In_{0.8})_2(CO_3)_3$	415	79
$(Co_{0.3}In_{0.8})_2(CO_3)_3$	410	80
$(Cu_{0.3}In_{0.8})_2(CO_3)_3$	416	81
$(Ti_{0.2}Bi_{0.8})_2(CO_3)_3$	342	78
$(Zn_{0.3}Bi_{0.6})_2(CO_3)_3$	331	77
$Ba_{0.2}Sn_{0.8}(HCO_3)_2$	452	92
$Ca_{0.2}Sn_{0.8}(HCO_3)_2$	441	94
$Sr_{0.2}Sn_{0.8}(HCO_3)_2$	443	94
$Mg_{0.2}Sn_{0.8}(HCO_3)_2$	451	93
$Mn_{0.2}Sn_{0.8}(HCO_3)_2$	443	91
$Fe_{0.2}Sn_{0.8}(HCO_3)_2$	439	92
$Co_{0.2}Sn_{0.8}(HCO_3)_2$	441	91
$Cu_{0.2}Sn_{0.8}(HCO_3)_2$	456	92
$Ti_{0.2}Sn_{0.7}(HCO_3)_2$	432	92
$Zn_{0.2}Sn_{0.8}(HCO_3)_2$	440	93
$Cr_{0.2}Sn_{0.7}(HCO_3)_2$	429	94
$Mo_{0.2}Sn_{0.8}(HCO_3)_2$	420	94
$Ba_{0.2}Pb_{0.8}(HCO_3)_2$	384	88
$Ca_{0.2}Pb_{0.8}(HCO_3)_2$	372	89
$Sr_{0.2}Pb_{0.8}(HCO_3)_2$	372	89
$Mg_{0.2}Pb_{0.8}(HCO_3)_2$	382	87
$Mn_{0.2}Pb_{0.8}(HCO_3)_2$	371	90
$Fe_{0.2}Pb_{0.8}(HCO_3)_2$	367	91
$Co_{0.2}Pb_{0.8}(HCO_3)_2$	371	90
$Cu_{0.2}Pb_{0.8}(HCO_3)_2$	379	89
$Ti_{0.2}Pb_{0.7}(HCO_3)_2$	352	89
$Zn_{0.2}Pb_{0.8}(HCO_3)_2$	368	90
$Cr_{0.2}Pb_{0.7}(HCO_3)_2$	369	90
$Mo_{0.2}Pb_{0.8}(HCO_3)_2$	357	91
$Fe_{0.3}In_{0.8}(HCO_3)_3$	365	86
$Co_{0.3}In_{0.8}(HCO_3)_3$	359	88
$Cu_{0.3}In_{0.8}(HCO_3)_3$	358	87
$Ti_{0.2}Bi_{0.8}(HCO_3)_3$	301	86
$Zn_{0.3}Bi_{0.8}(HCO_3)_3$	286	87

The batteries using the metal or semi-metal carbonate or hydrogencarbonate of Example 2 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogencarbonates has remarkably improved the cycle characteristics.

Example 3

The electrode characteristics of various metal and semi-metal hydrogenborates specified in Tables 6 through 8 and used as the anode active material were evaluated in Example 3.

Test cells discussed in Example 1 were manufactured, and the discharge capacities were measured under the same conditions as those of Example 1. The results of measurement are shown in Tables 6 through 8.

The measurement proved that all the test cells of Example 3 were capable of being charged and discharged.

After the conclusion of cathode polarization of these test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 3.

The above experiments show that cathode polarization makes lithium absorbed in the electrodes comprising the active materials of Example 3 and anode polarization makes the absorbed lithium released from the electrodes, thereby causing no deposit of metallic lithium.

Cylindrical batteries discussed in Example 1 were manufactured, and the capacity maintence rates at the 100-th cycle were measured under the same conditions as those of Example 1. The results of measurement are shown in Tables 6 through 8.

Table 6

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(HBO_3)_3$	305	78
$Al(H_2BO_3)_3$	294	80
$SnHBO_3$	532	83
$Sn(HBO_3)_2$	453	85
$Sn(H_2BO_3)_4$	405	86
$Sn(H_2BO_3)_2$	493	85
$Si(HBO_3)_2$	326	82
$Si(H_2BO_3)_4$	296	83
$PbHBO_3$	443	84
$Pb(H_2BO_3)_2$	421	86
$CdHBO_3$	328	84
$Bi_2(HBO_3)_3$	312	79
$Bi(H_2BO_3)_3$	289	81
$In_2(HBO_3)_3$	385	84
$In(H_2BO_3)_3$	368	86
$ZnHBO_3$	268	79
$Zn(H_2BO_3)_2$	268	81
$Ga_2(HBO_3)_3$	338	79
$Ga(H_2BO_3)_3$	312	82
$Ge(HBO_3)_2$	352	85
$Ge(H_2BO_3)_4$	335	87
$MgHBO_3$	296	84
$Mg(H_2BO_3)_2$	286	86

Table 7

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sb_2(HBO_3)_3$	310	80
$Ba_{0.1}Sn_{0.9}HBO_3$	486	84
$Ca_{0.1}Sn_{0.9}HBO_3$	482	85
$Sr_{0.1}Sn_{0.9}HBO_3$	482	85
$Mg_{0.1}Sn_{0.9}HBO_3$	479	84
$Zn_{0.1}Sn_{0.9}HBO_3$	481	86
$Cu_{0.1}Sn_{0.9}HBO_3$	469	87
$Co_{0.1}Sn_{0.9}HBO_3$	467	85
$Fe_{0.1}Sn_{0.9}HBO_3$	461	86
$Ni_{0.1}Sn_{0.9}HBO_3$	449	87
$Ti_{0.2}Sn_{0.7}HBO_3$	459	86
$Cr_{0.1}Sn_{0.7}HBO_3$	449	88
$V_{0.1}Sn_{0.9}HBO_3$	429	87
$Mo_{0.1}Sn_{0.9}HBO_3$	438	87
$W_{0.1}Sn_{0.8}HBO_3$	429	86
$(Mn_{0.3}In_{0.9})_2(HBO_3)_3$	352	82
$(Ni_{0.3}In_{0.8})_2(HBO_3)_3$	357	85
$(Co_{0.3}In_{0.8})_3(HBO_3)_3$	349	85
$(Mn_{0.3}Bi_{0.9})_2(HBO_3)_3$	291	82
$(Ni_{0.3}Bi_{0.8})_2(HBO_3)_3$	281	82
$(Co_{0.3}Bi_{0.8})_3(HBO_3)_3$	279	83

Table 8

Salt	Discharge capacity (mAg/g)	Capacity maintenance rate(%)
$Ba_{0.1}Pb_{0.9}HBO_3$	421	88
$Ca_{0.1}Pb_{0.9}HBO_3$	429	87
$Sr_{0.1}Pb_{0.9}HBO_3$	429	87
$Mg_{0.1}Pb_{0.9}HBO_3$	428	88
$Zn_{0.1}Pb_{0.9}HBO_3$	420	86
$Cu_{0.1}Pb_{0.9}HBO_3$	419	85
$Co_{0.1}Pb_{0.9}HBO_3$	425	84
$Fe_{0.1}Pb_{0.9}HBO_3$	422	85
$Ni_{0.1}Pb_{0.9}HBO_3$	428	86
$Ti_{0.2}Pb_{0.7}HBO_3$	419	89

Table 8 (continued)

Salt	Discharge capacity (mAg/g)	Capacity maintenance rate(%)
$Cr_{0.1}Pb_{0.7}HBO_3$	401	85
$V_{0.1}Pb_{0.9}HBO_3$	398	87
$Mo_{0.1}Pb_{0.9}HBO_3$	392	86
$W_{0.1}Pb_{0.8}HBO_3$	382	87

The batteries using the metal or semi-metal hydrogenborates of Example 3 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 4

The electrode characteristics of various salts of oxo-acides of sulfur specified in Tables 9 through 16 and used as the anode active material were evaluated in Example 4.

Tables 9 through 16 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 9

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(SO_4)_3$	389	82
$Al_2(SO_3)_3$	405	77
$Al_2(S_2O_7)_3$	342	83
$Al_2(SO_5)_3$	370	81
$Al_2(S_2O_8)_3$	338	85
$Al_2(S_2O_3)_3$	375	81
$Al_2(S_2O_6)_3$	364	82
$Al_2(S_2O_5)_3$	372	83
$Al_2(S_2O_2)_3$	378	83
$Al_2(S_2O_4)_3$	364	84
$Al_2(SO_2)_3$	415	80
$Sn(SO_4)_2$	482	85
$Sn(SO_3)_2$	521	80
$Sn(S_2O_7)_2$	416	86

Table 9-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sn(SO_5)_2$	456	83
$Sn(S_2O_8)_2$	403	84
$Sn(S_2O_3)_2$	456	82
$Sn(S_2O_6)_2$	423	88
$Sn(S_2O_5)_2$	437	87
$Sn(S_2O_2)_2$	464	84
$Sn(S_2O_4)_2$	424	86
$Sn(SO_2)_2$	510	82
$SnSO_4$	532	82
$SnSO_3$	556	79
SnS_2O_7	482	85
$SnSO_5$	502	83
$Al(HSO_4)_3$	356	91
$Al(HSO_3)_3$	375	87
$Al(HS_2O_7)_3$	320	92
$Al(HSO_5)_3$	335	91
$Al(HS_2O_8)_3$	314	89
$Al(HS_2O_3)_3$	316	88
$Al(HS_2O_6)_3$	352	89
$Al(HS_2O_5)_3$	346	90
$Al(HS_2O_2)_3$	348	91
$Al(HS_2O_4)_3$	334	92
$Al(HSO_2)_3$	358	89
$Sn(HSO_4)_4$	446	95
$Sn(HSO_3)_4$	453	92
$Sn(HS_2O_7)_4$	386	94
$Sn(HSO_5)_4$	423	93
$Sn(HS_2O_8)_4$	379	94
$Sn(HS_2O_3)_4$	433	93
$Sn(HS_2O_6)_4$	402	97
$Sn(HS_2O_5)_4$	410	96
$Sn(HS_2O_2)_4$	439	94
$Sn(HS_2O_4)_4$	403	95
$Sn(HSO_2)_4$	470	90
$Sn(HSO_4)_2$	486	93
$Sn(HSO_3)_2$	496	88
$Sn(HS_2O_7)_2$	450	92
$Sn(HSO_5)_2$	457	91

Table 10

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
SnS_2O_8	460	86
SnS_2O_3	505	79
SnS_2O_6	476	85
SnS_2O_5	483	85
SnS_2O_2	536	80
SnS_2O_4	497	81
$SnSO_2$	545	79
$Si(SO_4)_2$	395	85
$Si(SO_3)_2$	411	82
$Si(S_2O_7)_2$	341	87
$Si(SO_5)_2$	362	85
$Si(S_2O_6)_2$	322	87
$Si(S_2O_3)_2$	375	84
$Si(S_2O_6)_2$	332	85
$Si(S_2O_5)_2$	343	84
$Si(S_2O_2)_2$	378	82
$Si(S_2O_4)_2$	350	85
$Si(SO_2)_2$	421	83
$PbSO_4$	452	84
$PbSO_3$	472	83
PbS_2O_7	405	86
$PbSO_5$	432	85
PbS_2O_8	400	86
PbS_2O_3	441	84
PbS_2O_6	411	85
PbS_2O_5	419	85
PbS_2O_2	445	82
PbS_2O_4	412	84
$Sn(HS_2O_8)_2$	426	93
$Sn(HS_2O_3)_2$	472	91
$Sn(HS_2O_6)_2$	436	94
$Sn(HS_2O_5)_2$	440	94
$Sn(HS_2O_2)_2$	471	91
$Sn(HS_2O_4)_2$	446	93
$Sn(HSO_2)_2$	492	90
$Si(HSO_4)_4$	362	93
$Si(HSO_3)_4$	371	91
$Si(HS_2O_7)_4$	312	94
$Si(HSO_5)_4$	335	95
$Si(HS_2O_8)_4$	294	96

Table 10-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Si(HS_2O_3)_4$	341	93
$Si(HS_2O_6)_4$	309	95
$Si(HS_2O_5)_4$	312	94
$Si(HS_2O_2)_4$	340	92
$Si(HS_2O_4)_4$	318	93
$Si(HSO_2)_4$	390	90
$Pb(HSO_4)_2$	415	92
$Pb(HSO_3)_2$	426	91
$Pb(HS_2O_7)_2$	386	95
$Pb(HSO_5)_2$	403	94
$Pb(HS_2O_8)_2$	376	95
$Pb(HS_2O_3)_2$	411	94
$Pb(HS_2O_6)_2$	389	96
$Pb(HS_2O_5)_2$	399	95
$Pb(HS_2O_2)_2$	419	91
$Pb(HS_2O_4)_2$	391	93

Table 11

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$PbSO_2$	475	81
$CdSO_4$	414	79
$CdSO_3$	426	78
CdS_2O_7	378	81
$CdSO_5$	404	82
CdS_2O_8	369	84
CdS_2O_3	410	78
CdS_2O_6	398	79
CdS_2O_5	401	80
CdS_2O_2	410	78
CdS_2O_4	389	82
$CdSO_2$	420	76
$Bi_2(SO_4)_3$	364	76
$Bi_2(SO_3)_3$	381	75
$Bi_2(S_2O_7)_3$	324	79
$Bi_2(SO_5)_3$	348	78
$Bi_2(S_2O_8)_3$	315	81

Table 11-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Bi_2(S_2O_3)_3$	346	78
$Bi_2(S_2O_6)_3$	329	78
$Bi_2(S_2O_5)_3$	347	76
$Bi_2(S_2O_2)_3$	352	75
$Bi_2(S_2O_4)_3$	333	79
$Bi_2(SO_2)_3$	379	75
$In_2(SO_4)_3$	444	83
$In_2(SO_3)_3$	459	81
$In_2(S_2O_7)_3$	398	86
$In_2(SO_5)_3$	421	83
$In_2(S_2O_8)_3$	389	85
$Pb(HSO_2)_2$	435	91
$Cd(HSO_4)_2$	379	89
$Cd(HSO_3)_2$	398	88
$Cd(HS_2O_7)_2$	346	92
$Cd(HSO_5)_2$	382	93
$Cd(HS_2O_8)_2$	341	93
$Cd(HS_2O_3)_2$	379	90
$Cd(HS_2O_6)_2$	370	91
$Cd(HS_2O_5)_2$	374	93
$Cd(HS_2O_2)_2$	379	89
$Cd(HS_2O_4)_2$	365	93
$Cd(HSO_2)_2$	391	89
$Bi(HSO_4)_3$	337	87
$Bi(HSO_3)_3$	349	86
$Bi(HS_2O_7)_3$	298	87
$Bi(HSO_5)_3$	315	86
$Bi(HS_2O_8)_3$	276	90
$Bi(HS_2O_3)_3$	313	85
$Bi(HS_2O_6)_3$	298	86
$Bi(HS_2O_5)_3$	313	87
$Bi(HS_2O_2)_3$	321	84
$Bi(HS_2O_4)_3$	303	88
$Bi(HSO_2)_3$	336	86
$In(HSO_4)_3$	416	92
$In(HSO_3)_3$	420	91
$In(HS_2O_7)_3$	367	95
$In(HSO_5)_3$	390	94
$In(HS_2O_8)_3$	374	96

Table 12

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$In_2(S_2O_3)_3$	432	84
$In_2(S_2O_6)_3$	419	85
$In_2(S_2O_5)_3$	416	85
$In_2(S_2O_2)_3$	432	83
$In_2(S_2O_4)_3$	398	86
$In_2(SO_2)_3$	456	81
$ZnSO_4$	362	75
$ZnSO_3$	379	73
ZnS_2O_7	334	76
$ZnSO_5$	342	75
ZnS_2O_8	320	76
ZnS_2O_3	342	76
ZnS_2O_6	320	76
ZnS_2O_5	333	75
ZnS_2O_2	354	74
ZnS_2O_4	321	76
$ZnSO_2$	382	73
$MgSO_4$	333	81
$MgSO_3$	352	79
MgS_2O_7	298	84
$MgSO_5$	320	82
MgS_2O_8	302	83
MgS_2O_3	325	81
MgS_2O_6	300	83
MgS_2O_5	311	82
MgS_2O_2	328	82
MgS_2O_4	305	83
$MgSO_2$	342	79
$In(HS_2O_3)_3$	400	95
$In(HS_2O_6)_3$	381	95
$In(HS_2O_5)_3$	390	95
$In(HS_2O_2)_3$	402	91
$In(HS_2O_4)_3$	370	95
$In(HSO_2)_3$	420	92
$Zn(HSO_4)_2$	333	85
$Zn(HSO_3)_2$	342	84
$Zn(HS_2O_7)_2$	300	87
$Zn(HSO_6)_2$	312	86
$Zn(HS_2O_8)_2$	294	85
$Zn(HS_2O_3)_2$	310	85
$Zn(HS_2O_6)_2$	300	84
$Zn(HS_2O_5)_2$	310	86
$Zn(HS_2O_2)_2$	325	84

Table 12-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Zn(HS_2O_4)_2$	290	86
$Zn(HSO_2)_2$	341	84
$Mg(HSO_4)_2$	312	91
$Mg(HSO_3)_2$	330	89
$Mg(HS_2O_7)_2$	271	93
$Mg(HSO_5)_2$	294	92
$Mg(HS_2O_8)_2$	279	93
$Mg(HS_2O_3)_2$	293	92
$Mg(HS_2O_6)_2$	276	94
$Mg(HS_2O_5)_2$	288	92
$Mg(HS_2O_2)_2$	296	93
$Mg(HS_2O_4)_2$	276	94
$Mg(HSO_2)_2$	302	90

Table 13

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ga_2(SO_4)_3$	364	76
$Ga_2(SO_3)_3$	382	74
$Ga_2(S_2O_7)_3$	321	79
$Ga_2(SO_5)_3$	352	75
$Ga_2(S_2O_8)_3$	312	77
$Ga_2(S_2O_3)_3$	352	75
$Ga_2(S_2O_6)_3$	333	76
$Ga_2(S_2O_5)_3$	342	75
$Ga_2(S_2O_2)_3$	354	74
$Ga_2(S_2O_4)_3$	326	76
$Ga_2(SO_2)_3$	375	73
$Ge(SO_4)_2$	431	78
$Ge(SO_3)_2$	449	75
$Ge(S_2O_7)_2$	395	81
$Ge(SO_5)_2$	423	78
$Ge(S_2O_8)_2$	386	81
$Ge(S_2O_3)_2$	425	77
$Ge(S_2O_6)_2$	401	80

Table 13-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ge(S_2O_5)_2$	408	79
$Ge(S_2O_2)_2$	420	79
$Ge(S_2O_4)_2$	390	82
$Ge(SO_2)_2$	435	77
$Cr_2(SO_4)_3$	353	81
$Cr_2(SO_3)_3$	369	80
$W(SeO_4)_2$	298	79
$CoSO_4$	352	82
$CoSO_3$	362	80
$NiSO_4$	349	81
$Ga(HSO_4)_3$	339	86
$Ga(HSO_3)_3$	352	85
$Ga(HS_2O_7)_3$	301	88
$Ga(HSO_5)_3$	315	84
$Ga(HS_2O_8)_3$	294	86
$Ga(HS_2O_3)_3$	321	87
$Ga(HS_2O_6)_3$	303	87
$Ga(HS_2O_5)_3$	318	86
$Ga(HS_2O_2)_3$	321	86
$Ga(HS_2O_4)_3$	296	84
$Ga(HSO_2)_3$	348	84
$Ge(HSO_4)_4$	412	89
$Ge(HSO_3)_4$	421	86
$Ge(HS_2O_7)_4$	370	92
$Ge(HSO_5)_4$	396	90
$Ge(HS_2O_8)_4$	356	93
$Ge(HS_2O_3)_4$	387	85
$Ge(HS_2O_6)_4$	374	88
$Ge(HS_2O_5)_4$	373	87
$Ge(HS_2O_2)_4$	395	89
$Ge(HS_2O_4)_4$	365	93
$Ge(HSO_2)_4$	402	89
$Cr(HSO_4)_3$	325	92
$Cr(HSO_3)_3$	341	90
$W(HSO_4)_4$	275	89
$Co(HSO_4)_2$	321	92
$Co(HSO_3)_2$	329	90
$Ni(HSO_4)_2$	319	90

Table 14

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$NiSO_3$	354	79
$CuSO_4$	326	82
$CuSO_3$	340	80
$Ti_2(SO_4)_3$	315	83
$Mo_2(SO_4)_3$	324	84
VSO_4	306	83
$MnSO_4$	345	82
$MnSO_3$	356	80
$FeSO_4$	354	81
$FeSO_3$	362	78
$Nb_2(SO_4)_5$	257	82
$CaSO_4$	398	78
$CaSO_3$	405	76
$SrSO_4$	398	78
$SrSO_3$	405	76
$BaSO_4$	375	79
$BaSO_3$	386	78
$Ni(HSO_3)_2$	326	88
$Cu(HSO_4)_2$	301	93
$Cu(HSO_3)_2$	319	91
$Ti(HSO_4)_3$	284	90
$Mo(HSO_4)_3$	299	92
$V(HSO_4)_2$	274	92
$Mn(HSO_4)_2$	315	93
$Mn(HSO_3)_2$	320	90
$Fe(HSO_4)_2$	327	91
$Fe(HSO_3)_2$	333	89
$Nb(HSO_4)_5$	229	90
$Ca(HSO_4)_2$	375	87
$Ca(HSO_3)_2$	381	85
$Sr(HSO_4)_2$	375	87
$Sr(HSO_3)_2$	381	85
$Ba(HSO_4)_2$	352	87
$Ba(HSO_3)_2$	360	86

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Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Mg_{0.1}Sn_{0.9}SO_4$	503	84
$Sr_{0.1}Sn_{0.9}SO_4$	503	84
$Ca_{0.1}Sn_{0.9}SO_4$	503	84
$Zn_{0.1}Sn_{0.9}SO_4$	500	85
$Ni_{0.1}Sn_{0.9}SO_4$	495	84
$Fe_{0.1}Sn_{0.9}SO_4$	492	86
$Co_{0.1}Sn_{0.9}SO_4$	489	87
$Mn_{0.1}Sn_{0.9}SO_4$	482	86
$Cu_{0.1}Sn_{0.9}SO_4$	485	85
$Mo_{0.1}Sn_{0.9}SO_4$	476	84
$V_{0.1}Sn_{0.9}SO_4$	473	86
$W_{0.1}Sn_{0.8}SO_4$	459	83
$Cr_{0.2}Sn_{0.7}SO_4$	476	84
$Mo_{0.2}Sn_{0.7}SO_4$	476	85
$Mg_{0.1}Pb_{0.9}SO_4$	420	86
$Sr_{0.1}Pb_{0.9}SO_4$	420	86
$Ca_{0.1}Pb_{0.9}SO_4$	420	86
$Zn_{0.1}Pb_{0.9}SO_4$	421	87
$Ni_{0.1}Pb_{0.9}SO_4$	415	86
$Fe_{0.1}Pb_{0.9}SO_4$	410	87
$Co_{0.1}Pb_{0.9}SO_4$	416	88
$Mn_{0.1}Pb_{0.9}SO_4$	408	86
$Cu_{0.1}Pb_{0.9}SO_4$	406	87
$Mo_{0.1}Pb_{0.9}SO_4$	398	85
$V_{0.1}Pb_{0.9}SO_4$	387	85
$W_{0.1}Pb_{0.8}SO_4$	376	85
$Cr_{0.2}Pb_{0.7}SO_4$	387	84
$Mo_{0.2}Pb_{0.7}SO_4$	389	85
$Mg_{0.1}Sn_{0.9}(HSO_4)_2$	481	94
$Sr_{0.1}Sn_{0.9}(HSO_4)_2$	481	94
$Ca_{0.1}Sn_{0.9}(HSO_4)_2$	481	94
$Zn_{0.1}Sn_{0.9}(HSO_4)_2$	479	95
$Ni_{0.1}Sn_{0.9}(HSO_4)_2$	470	95
$Fe_{0.1}Sn_{0.9}(HSO_4)_2$	476	95
$Co_{0.1}Sn_{0.9}(HSO_4)_2$	469	94
$Mn_{0.1}Sn_{0.9}(HSO_4)_2$	465	96
$Cu_{0.1}Sn_{0.9}(HSO_4)_2$	462	94
$Mo_{0.1}Sn_{0.9}(HSO_4)_2$	459	95
$V_{0.1}Sn_{0.9}(HSO_4)_2$	451	95
$W_{0.1}Sn_{0.8}(HSO_4)_2$	432	94
$Cr_{0.2}Sn_{0.7}(HSO_4)_2$	455	94

Table 15-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Mo_{0.2}Sn_{0.7}(HSO_4)_2$	452	95
$Mg_{0.1}Pb_{0.9}(HSO_4)_2$	394	95
$Sr_{0.1}Pb_{0.9}(HSO_4)_2$	394	95
$Ca_{0.1}Pb_{0.9}(HSO_4)_2$	394	95
$Zn_{0.1}Pb_{0.9}(HSO_4)_2$	394	94
$Ni_{0.1}Pb_{0.9}(HSO_4)_2$	384	97
$Fe_{0.1}Pb_{0.9}(HSO_4)_2$	381	95
$Co_{0.1}Pb_{0.9}(HSO_4)_2$	384	96
$Mn_{0.1}Pb_{0.9}(HSO_4)_2$	381	95
$Cu_{0.1}Pb_{0.9}(HSO_4)_2$	386	96
$Mo_{0.1}Pb_{0.9}(HSO_4)_2$	370	95
$V_{0.1}Pb_{0.9}(HSO_4)_2$	368	94
$W_{0.1}Pb_{0.9}(HSO_4)_2$	359	95
$Cr_{0.2}Pb_{0.7}(HSO_4)_2$	364	94
$Mo_{0.2}Pb_{0.7}(HSO_4)_2$	368	94

Table 16

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$(Mg_{0.3}In_{0.8})_2(SO_4)_3$	410	85
$(Zn_{0.3}In_{0.8})_2(SO_4)_3$	406	86
$(Ni_{0.3}In_{0.8})_2(SO_4)_3$	398	86
$(Co_{0.3}Bi_{0.8})_2(SO_4)_3$	333	80
$(Fe_{0.3}Bi_{0.8})_2(SO_4)_3$	325	82
$(Mn_{0.3}Bi_{0.8})_2(SO_4)_3$	330	80
$Sn(SO_4)_{0.5}(HSO_4)$	498	90
$Pb(SO_4)_{0.5}(HSO_4)$	425	90
$In_2(SO_4)_{2.5}(HSO_4)$	425	90
$Bi_2(SO_4)_{2.5}(HSO_4)$	343	84
$Co_{0.3}In_{0.8}(HSO_4)_3$	379	94
$Fe_{0.3}In_{0.8}(HSO_4)_3$	370	95
$Mn_{0.3}In_{0.8}(HSO_4)_3$	368	95
$Mg_{0.3}Bi_{0.8}(HSO_4)_3$	298	90
$Zn_{0.3}Bi_{0.8}(HSO_4)_3$	289	89
$Ni_{0.3}Bi_{0.8}(HSO_4)_3$	295	91
$Sn(SO_4)_{0.9}(HSO_4)_{0.2}$	519	86

Table 16 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Pb(SO_4)_{0.9}(HSO_4)_{0.2}$	438	87
$In_2(SO_4)_{2.9}(HSO_4)_{0.2}$	438	86
$Bi_2(SO_4)_{2.9}(HSO_4)_{0.2}$	350	80

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 4.

The batteries using the metal or semi-metal sulfate, sulfite, disulfate, peroxomonosulfate, peroxodisulfate, thiosulfate, disulfite, thiosulfite, hydrogensulfate, thionate, or sulfoxylate of Example 4 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogensulfates has remarkably improved the cycle characteristics.

Example 5

The electrode characteristics of various salts of oxo-acids of selenium specified in Tables 17 through 20 and used as the anode active material were evaluated in Example 5.

Tables 17 through 20 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 17

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(SeO_4)_3$	362	83
$Al_2(SeO_3)_3$	387	80
$Sn(SeO_4)_2$	462	84
$Sn(SeO_3)_2$	483	81
$SnSeO_4$	512	83
$SnSeO_3$	521	80
Sn_2SeO_5	534	79
$Si(SeO_4)_2$	364	84
$Si(SeO_3)_2$	379	80
$PbSeO_4$	432	85
$PbSeO_3$	445	82
Pb_2SeO_5	498	80
$CdSeO_4$	386	80
$CdSeO_3$	399	78
$Bi_2(SeO_4)_3$	339	77
$Bi_2(SeO_3)_3$	349	72
$In_2(SeO_4)_3$	421	85
$In_2(SeO_3)_3$	438	83
$ZnSeO_4$	339	74
$ZnSeO_3$	348	70
$MgSeO_4$	310	82
$MgSeO_3$	321	79
$Ga_2(SeO_4)_3$	339	75
$Ga_2(SeO_3)_3$	349	73
$Ge(SeO_4)_2$	405	77
$Ge(SeO_3)_2$	420	72
$Al(HSeO_4)_3$	341	92
$Al(HSeO_3)_3$	367	89
$Sn(HSeO_4)_4$	442	92
$Sn(HSeO_3)_4$	462	93
$Sn(HSeO_4)_2$	489	94
$Sn(HSeO_3)_2$	501	90
$SnSeO_5$	508	84
$Si(HSeO_4)_4$	342	92
$Si(HSeO_3)_4$	347	90
$Pb(HSeO_4)_2$	412	93
$Pb(HSeO_3)_2$	421	92
$PbSeO_5$	425	85
$Cd(HSeO_4)_2$	364	90
$Cd(HSeO_3)_2$	374	88
$Bi(HSeO_4)_3$	314	89
$Bi(HSeO_3)_3$	321	86

Table 17-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$In(HSeO_4)_3$	397	94
$In(HSeO_3)_3$	409	93
$Zn(HSeO_4)_2$	315	85
$Zn(HSeO_3)_2$	320	83
$Mg(HSeO_4)_2$	289	92
$Mg(HSeO_3)_2$	301	87
$Ga(HSeO_4)_3$	314	86
$Ga(HScO_3)_3$	324	84
$Ge(HSeO_4)_4$	385	86
$Ge(HSeO_3)_4$	396	83

Table 18

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Cr_2(SeO_4)_3$	321	75
$Cr_2(SeO_3)_3$	331	76
$W(SeO_4)_2$	257	72
$CoSeO_4$	286	73
$CoSeO_3$	297	76
$NiSeO_4$	286	76
$NiSeO_3$	299	76
$CuSeO_4$	287	73
$CuSeO_3$	289	74
$Ti_2(SeO_4)_3$	253	77
$Mo_2(SeO_4)_3$	223	73
$VSeO_4$	282	79
$MnSeO_4$	265	73
$MnSeO_3$	276	75
$FeSeO_4$	282	74
$FeSeO_3$	293	75
$Nb_2(SeO_4)_5$	215	75
$CaSeO_4$	321	74
$CaSeO_3$	334	76
$SrSeO_3$	334	76
$BaSeO_4$	345	73
$BaSeO_3$	353	74
$Sb_2(SeO_4)_3$	364	72

Table 18-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ir_2(SeO_4)_3$	345	73
$Cr(HSeO_4)_3$	305	84
$Cr(HSeO_3)_3$	314	86
$W(HSeO_4)_4$	234	83
$Co(HSeO_4)_2$	261	82
$Co(HSeO_3)_2$	271	85
$Ni(HSeO_4)_2$	264	84
$Ni(HSeO_3)_2$	274	85
$Cu(HSeO_4)_2$	264	84
$Cu(HSeO_3)_2$	259	84
$Ti(HSeO_4)_3$	230	86
$Mo(HSeO_4)_3$	201	84
$V(HSeO_4)_2$	261	89
$Mn(HSeO_4)_2$	241	82
$Mn(HSeO_3)_2$	251	84
$Fe(HSeO_4)_2$	260	86
$Fe(HSeO_3)_2$	271	85
$Nb(HSeO_4)_5$	195	84
$Ca(HSeO_4)_2$	301	82
$Ca(HSeO_3)_2$	309	85
$Sr(HSeO_3)_2$	309	85
$Ba(HSeO_4)_2$	314	84
$Ba(HSeO_3)_2$	321	83
$Sb(HSeO_4)_3$	335	86
$Ir(HSeO_4)_3$	315	85

Table 19

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Mg_{0.1}Sn_{0.9}SeO_4$	486	85
$Zn_{0.1}Sn_{0.9}SeO_4$	484	86
$Ni_{0.1}Sn_{0.9}SeO_4$	472	85
$Fe_{0.1}Sn_{0.9}SeO_4$	471	86
$Co_{0.1}Sn_{0.9}SeO_4$	476	87
$Mn_{0.1}Sn_{0.9}SeO_4$	483	84
$Cu_{0.1}Sn_{0.9}SeO_4$	475	85
$Mo_{0.1}Sn_{0.9}SeO_4$	465	86
$V_{0.1}Sn_{0.9}SeO_4$	459	88
$W_{0.1}Sn_{0.9}SeO_4$	443	88
$Cr_{0.3}Sn_{0.7}SeO_4$	433	86
$Ca_{0.1}Sn_{0.9}SeO_4$	492	85

Table 19-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sr_{0.1}Sn_{0.9}SeO_4$	492	85
$Ba_{0.1}Sn_{0.9}SeO_4$	475	86
$Mg_{0.1}Pb_{0.9}SeO_4$	415	85
$Zn_{0.1}Pb_{0.9}SeO_4$	409	86
$Ni_{0.1}Pb_{0.9}SeO_4$	414	87
$Fe_{0.1}Pb_{0.9}SeO_4$	401	88
$Co_{0.1}Pb_{0.9}SeO_4$	405	86
$Mn_{0.1}Pb_{0.9}SeO_4$	403	84
$Cu_{0.1}Pb_{0.9}SeO_4$	402	85
$Mo_{0.1}Pb_{0.9}SeO_4$	394	85
$V_{0.1}Pb_{0.9}SeO_4$	396	84
$W_{0.1}Pb_{0.9}SeO_4$	379	86
$Cr_{0.2}Pb_{0.7}SeO_4$	368	85
$Ca_{0.1}Pb_{0.9}SeO_4$	408	85
$Sr_{0.1}Pb_{0.9}SeO_4$	408	85
$Ba_{0.1}Pb_{0.9}SeO_4$	381	86
$Mg_{0.1}Sn_{0.9}(HSeO_4)_2$	453	94
$Zn_{0.1}Sn_{0.9}(HSeO_4)_2$	461	96
$Ni_{0.1}Sn_{0.9}(HSeO_4)_2$	453	95
$Fe_{0.1}Sn_{0.9}(HSeO_4)_2$	449	94
$Co_{0.1}Sn_{0.9}(HSeO_4)_2$	448	95
$Mn_{0.1}Sn_{0.9}(HSeO_4)_2$	457	92
$Cu_{0.1}Sn_{0.9}(HSeO_4)_2$	453	94
$Mo_{0.1}Sn_{0.9}(HSeO_4)_2$	441	95
$V_{0.1}Sn_{0.9}(HSeO_4)_2$	432	97
$W_{0.1}Sn_{0.9}(HSeO_4)_2$	420	96
$Cr_{0.2}Sn_{0.7}(HSeO_4)_2$	416	95
$Ca_{0.1}Sn_{0.9}(HSeO_4)_2$	470	95
$Sr_{0.1}Sn_{0.9}(HSeO_4)_2$	470	95
$Ba_{0.1}Sn_{0.9}(HSeO_4)_2$	448	94
$Mg_{0.1}Pb_{0.9}(HSeO_4)_2$	385	94
$Zn_{0.1}Pb_{0.9}(HSeO_4)_2$	389	95
$Ni_{0.1}Pb_{0.9}(HSeO_4)_2$	391	96
$Fe_{0.1}Pb_{0.9}(HSeO_4)_2$	371	98
$Co_{0.1}Pb_{0.9}(HSeO_4)_2$	379	95
$Mn_{0.1}Pb_{0.9}(HSeO_4)_2$	371	95
$Cu_{0.1}Pb_{0.9}(HSeO_4)_2$	376	96
$Mo_{0.1}Pb_{0.9}(HSeO_4)_2$	370	94
$V_{0.1}Pb_{0.9}(HSeO_4)_2$	369	95
$W_{0.1}Pb_{0.9}(HSeO_4)_2$	349	97
$Cr_{0.2}Pb_{0.7}(HSeO_4)_2$	333	96
$Ca_{0.1}Pb_{0.9}(HSeO_4)_2$	379	94
$Sr_{0.1}Pb_{0.9}(HSeO_4)_2$	379	94
$Ba_{0.1}Pb_{0.9}(HSeO_4)_2$	353	96

Table 20

Salt	Discharge capacity (mAh/g)	Capacity maintenarate rate(%)
$(Mg_{0.3}In_{0.8})_2(SeO_4)_3$	398	86
$(Zn_{0.3}In_{0.8})_2(SeO_4)_3$	387	87
$(Ni_{0.3}In_{0.8})_2(SeO_4)_3$	379	86
$(Co_{0.3}Bi_{0.8})_2(SeO_4)_3$	318	80
$(Fe_{0.3}Bi_{0.8})_2(SeO_4)_3$	310	82
$(Mn_{0.3}Bi_{0.8})_2(SeO_4)_3$	320	82
$Co_{0.3}In_{0.8}(HSeO_4)_3$	374	95
$Fe_{0.3}In_{0.8}(HSeO_4)_3$	361	98
$Mn_{0.3}In_{0.8}(HSeO_4)_3$	348	96
$Mg_{0.3}Bi_{0.8}(HSeO_4)_3$	279	91
$Zn_{0.3}Bi_{0.8}(HSeO_4)_3$	284	92
$Ni_{0.3}Bi_{0.8}(HSeO_4)_3$	298	93

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 5.

The batteries using the metal or semi-metal selenate, selenite, hydrogenselenate, or hydrogenselenite of Example 5 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogenselenates and hydrogenselenites has remarkably improved the cycle characteristics.

Example 6

The electrode characteristics of various salts of oxo-acids of tellurium specified in Tables 21 through 23 and used as the anode active material were evaluated in Example 6.

Tables 21 through 23 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 21

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(TeO_4)_3$	346	82
$SnTeO_4$	426	84
$SnTe_3O_8$	385	87
Sn_3TeO_6	489	85
$Si(TeO_4)_2$	337	83
$PbTeO_4$	405	84
$PbTe_3O_8$	352	85
Pb_3TeO_6	453	82
$CdTeO_4$	354	79
$Bi_2(TeO_4)_3$	314	79
Bi_2TeO_6	345	77
$In_2(TeO_4)_3$	384	82
In_2TeO_6	405	80
Sb_2TeO_6	384	78
Ir_2TeO_6	351	78
$ZnTeO_4$	302	75
$MgTeO_4$	289	81
Ga_2TeO_6	314	74
$Ge(TeO_4)_2$	370	75
Ti_2TeO_6	221	78
Cr_2TeO_6	287	74
$NiTeO_4$	253	76
$FeTeO_4$	254	75
$MnTeO_4$	247	74
$CoTeO_4$	253	75
$VTeO_4$	241	76
$CuTeO_4$	251	75
$Al(HTeO_4)_3$	319	89
$Sn(HTeO_4)_2$	397	90
SnH_4TeO_6	359	95

Table 21-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sn_2H_2TeO_6$	459	94
$Si(HTeO_4)_4$	307	93
$Pb(HTcO_4)_2$	372	92
PbH_4TeO_6	321	94
$Pb_2H_2TeO_6$	426	93
$Cd(HTeO_4)_2$	320	90
$Bi(HTeO_4)_3$	284	87
BiH_3TeO_6	314	87
$In(HTeO_4)_3$	359	89
InH_3TeO_6	374	90
SbH_3TeO_6	352	89
IrH_3TeO_6	321	88
$Zn(HTcO_4)_2$	275	86
$Mg(HSeO_4)_2$	264	89
GaH_3TeO_6	275	86
$Ge(HTeO_4)_4$	342	86
TiH_3TeO_6	198	87
CrH_3TeO_6	255	86
$Ni(HTeO_4)_2$	234	87
$Fe(HSeO_4)_2$	229	86
$Mn(HTeO_4)_2$	219	85
$Co(HSeO_4)_2$	218	85
$V(HTeO_4)_2$	214	87
$Cu(HTeO_4)_2$	216	85

Table 22

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$MoTeO_4$	234	73
$W(TeO_4)_2$	215	73
$CaTeO_4$	315	74
$SrTeO_4$	315	74
$BaTeO_4$	305	75
$Mg_{0.1}Sn_{0.9}TeO_4$	402	86
$Ca_{0.1}Sn_{0.9}TeO_4$	402	86
$Sr_{0.1}Sn_{0.9}TeO_4$	402	86
$Zn_{0.1}Sn_{0.9}TeO_4$	405	85
$Ni_{0.1}Sn_{0.9}TeO_4$	400	86
$Fe_{0.1}Sn_{0.9}TeO_4$	398	87
$Co_{0.1}Sn_{0.9}TeO_4$	396	86
$Mn_{0.1}Sn_{0.9}TeO_4$	389	85
$Cu_{0.1}Sn_{0.9}TeO_4$	390	85
$Mo_{0.1}Sn_{0.9}TeO_4$	379	87

Table 22-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$V_{0.1}Sn_{0.9}TeO_4$	378	88
$W_{0.1}Sn_{0.8}TeO_4$	369	85
$Cr_{0.2}Sn_{0.7}TeO_4$	374	86
$Mg_{0.1}Pb_{0.9}TeO_4$	375	86
$Ca_{0.1}Pb_{0.9}TeO_4$	375	86
$Sr_{0.1}Pb_{0.9}TeO_4$	375	86
$Zn_{0.1}Pb_{0.9}TeO_4$	379	85
$Ni_{0.1}Pb_{0.9}TeO_4$	370	87
$Fe_{0.1}Pb_{0.9}TeO_4$	367	88
$Co_{0.1}Pb_{0.9}TeO_4$	368	87
$Mn_{0.1}Pb_{0.9}TeO_4$	364	86
$Cu_{0.1}Pb_{0.9}TeO_4$	362	87
$Mo_{0.1}Pb_{0.9}TeO_4$	354	87
$V_{0.1}Pb_{0.9}TeO_4$	352	86
$W_{0.1}Pb_{0.8}TeO_4$	341	85
$Mo(HTeO_4)_2$	215	81
$W(HTeO_4)_4$	185	82
$Ca(HTeO_4)_2$	289	84
$Sr(HTeO_4)_2$	289	84
$Ba(HTeO_4)_2$	279	83
$Mg_{0.1}Sn_{0.9}(HTeO_4)_2$	375	95
$Ca_{0.1}Sn_{0.9}(HTeO_4)_2$	375	95
$Sr_{0.1}Sn_{0.9}(HTeO_4)_2$	375	95
$Zn_{0.1}Sn_{0.9}(HTeO_4)_2$	379	94
$Ni_{0.1}Sn_{0.9}(HTeO_4)_2$	374	95
$Fe_{0.1}Sn_{0.9}(HTeO_4)_2$	370	96
$Co_{0.1}Sn_{0.9}(HTeO_4)_2$	375	95
$Mn_{0.1}Sn_{0.9}(HTeO_4)_2$	369	94
$Cu_{0.1}Sn_{0.9}(HTeO_4)_2$	371	94
$Mo_{0.1}Sn_{0.9}(HTeO_4)_2$	352	95
$V_{0.1}Sn_{0.9}(HTeO_4)_2$	349	97
$W_{0.1}Sn_{0.8}(HTeO_4)_2$	342	95
$Cr_{0.2}Sn_{0.7}(HTeO_4)_2$	344	94
$Mg_{0.1}Pb_{0.9}(HTeO_4)_2$	335	95
$Ca_{0.1}Pb_{0.9}(HTeO_4)_2$	335	95
$Sr_{0.1}Pb_{0.9}(HTeO_4)_2$	335	95
$Zn_{0.1}Pb_{0.9}(HTeO_4)_2$	339	94
$Ni_{0.1}Pb_{0.9}(HTeO_4)_2$	348	95
$Fe_{0.1}Pb_{0.9}(HTeO_4)_2$	332	96
$Co_{0.1}Pb_{0.9}(HTeO_4)_2$	321	95
$Mn_{0.1}Pb_{0.9}(HTeO_4)_2$	322	94
$Cu_{0.1}Pb_{0.9}(HTeO_4)_2$	337	95
$Mo_{0.1}Pb_{0.9}(HTeO_4)_2$	326	94
$V_{0.1}Pb_{0.9}(HTeO_4)_2$	322	95
$W_{0.1}Pb_{0.8}(HTeO_4)_2$	320	96

Table 23

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Cr_{0.2}Pb_{0.7}TeO_4$	361	84
$(Mg_{0.3}In_{0.8})_2TeO_6$	374	82
$(Zn_{0.3}In_{0.8})_2TeO_6$	370	83
$(Fe_{0.3}In_{0.8})_2TeO_6$	364	84
$(Mg_{0.3}Bi_{0.8})_2TeO_6$	315	79
$(Zn_{0.3}Bi_{0.8})_2TeO_6$	318	80
$(Fe_{0.3}Bi_{0.8})_2TeO_6$	308	81
$Cr_{0.2}Pb_{0.7}(HTeO_4)_2$	337	93
$Cr_{0.3}In_{0.8}H_3TeO_6$	351	93
$Ni_{0.3}In_{0.8}H_3TeO_6$	341	92
$Mn_{0.3}In_{0.8}H_3TeO_6$	338	92
$Co_{0.3}Bi_{0.8}H_3TeO_6$	287	88
$Ni_{0.3}Bi_{0.8}H_3TeO_6$	286	90
$Mn_{0.3}Bi_{0.8}H_3TeO_6$	279	90

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 6.

The batteries using the metal or semi-metal tellurate or hydrogentellurate of Example 6 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides. Especially the use of hydrogentellurates has remarkably improved the cycle characteristics.

Example 7

The electrode characteristics of various metal and semi-metal hydrogenphosphates, phosphinates, and phosphonates specified in Tables 24 through 27 and used as the anode active material were evaluated in Example 7.

Tables 24 through 27 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 24

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al(PH_2O_2)_3$	366	83
$Al_2(PHO_3)_3$	353	84
$Al_2(HPO_4)_3$	348	85
$Al(H_2PO_4)_3$	315	87
$Sn(PH_2O_2)_4$	412	88
$Sn(PHO_3)_2$	455	89
$Sn(HPO_4)_2$	452	88
$Sn(H_2PO_4)_4$	384	89
$Sn(PH_2O_2)_2$	452	82

Table 24 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$SnPHO_3$	486	92
$SnHPO_4$	485	95
$Sn(H_2PO_4)_2$	402	86
$Si(PH_2O_2)_4$	304	85
$Si(PHO_3)_2$	332	86
$Bi(PH_2O_2)_3$	333	82
$Bi_2(PHO_3)_3$	345	83
$Bi_2(HPO_4)_3$	340	83
$Bi(H_2PO_4)_3$	324	85
$In(PH_2O_2)_3$	365	82
$In_2(PHO_3)_3$	380	81
$In_2(HPO_4)_3$	377	83
$In(H_2PO_4)_3$	333	86
$Zn(PH_2O_2)_2$	298	83
$ZnPHO_3$	298	83
$ZnHPO_4$	295	83
$Zn(H_2PO_4)_2$	264	84
$Mg(PH_2O_2)_2$	281	84
$MgPHO_3$	288	83

Table 25

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Si(HPO_4)_2$	322	87
$Si(H_2PO_4)_2$	285	88
$Pb(PH_2O_2)_2$	420	85
$PbPHO_3$	425	85
$PbHPO_4$	418	89
$Pb(H_2PO_4)_2$	405	90
$Cd(PH_2O_2)_2$	380	82
$CdPHO_3$	385	83
$CdHPO_4$	384	83
$Cd(H_2PO_4)_2$	375	86
$Sb_2(HPO_4)_3$	321	82
$Ti_2(HPO_4)_3$	275	84
$V_2(HPO_4)_3$	250	85

Table 25 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Cr_2(HPO_4)_3$	284	84
$Mn_2(HPO_4)_3$	275	85
$MgHPO_4$	286	84
$Mg(H_2PO_4)_2$	267	87
$Ga(PH_2O_2)_3$	321	82
$Ga_2(PHO_3)_3$	335	83
$Ga_2(HPO_4)_3$	325	84
$Ga(H_2PO_4)_3$	305	86
$Ge(PH_2O_2)_4$	367	83
$Ge(PHO_3)_2$	382	84
$Ge(HPO_4)_2$	375	87
$Ge(H_2PO_4)_4$	342	89
$Fe_2(HPO_4)_3$	264	85
$CoHPO_4$	264	84
$NiHPO_4$	261	84
$CuHPO_4$	275	85

Table 26

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$SrHPO_4$	332	85
$Ca_{0.2}Sn_{0.8}HPO_4$	451	88
$Sr_{0.2}Sn_{0.8}HPO_4$	451	88
$Ba_{0.2}Sn_{0.8}HPO_4$	432	89
$Zn_{0.2}Sn_{0.8}HPO_4$	437	92
$Fe_{0.2}Sn_{0.8}HPO_4$	441	91
$Ni_{0.2}Sn_{0.8}HPO_4$	438	92
$Co_{0.2}Sn_{0.8}HPO_4$	442	92
$Mn_{0.2}Sn_{0.8}HPO_4$	429	90
$Ti_{0.2}Sn_{0.7}HPO_4$	415	91
$Cu_{0.2}Sn_{0.8}HPO_4$	429	92
$Cr_{0.2}Sn_{0.7}HPO_4$	418	93
$V_{0.2}Sn_{0.8}HPO_4$	404	91
$W_{0.1}Sn_{0.8}HPO_4$	406	90
$BaHPO_4$	312	86
$Ca_{0.2}Pb_{0.8}HPO_4$	372	90

Table 26 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sr_{0.2}Pb_{0.8}HPO_4$	372	90
$Ba_{0.2}Pb_{0.8}HPO_4$	359	91
$Zn_{0.2}Pb_{0.8}HPO_4$	382	93
$Fe_{0.2}Pb_{0.8}HPO_4$	374	94
$Ni_{0.2}Pb_{0.8}HPO_4$	368	93
$Co_{0.2}Pb_{0.8}HPO_4$	376	92
$Mn_{0.2}Pb_{0.8}HPO_4$	374	93
$Ti_{0.2}Pb_{0.7}HPO_4$	369	94
$Cu_{0.2}Pb_{0.8}HPO_4$	371	93
$Cr_{0.2}Pb_{0.7}HPO_4$	368	95
$V_{0.2}Pb_{0.8}HPO_4$	365	93
$W_{0.1}Pb_{0.8}HPO_4$	345	93

Table 27

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sn_2(P_2O_7)_{0.9}(HPO_4)_{0.2}$	495	82
$Sn_2(P_2O_7)_{0.8}(HPO_4)_{0.4}$	490	88
$Pb_2(P_2O_7)_{0.9}(HPO_4)_{0.2}$	425	80
$Pb_2(P_2O_7)_{0.8}(HPO_4)_{0.4}$	422	82

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 7.

The batteries using the metal or semi-metal hydrogenphosphate, phosphinate, or phosphonate of Example 7 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 8

The electrode characteristics of various metal and semi-metal cyanides, cyanates, and thiocyanates specified in Tables 28 through 30 and used as the anode active material were evaluated in Example 8.

Tables 28 through 30 show the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 28

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al(CN)_3$	382	76
$Al(SCN)_3$	286	82
$Al(ONC)_3$	364	80

Table 28 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Sn(CN)_4$	529	85
$Sn(SCN)_4$	326	92
$Sn(ONC)_4$	436	90
$Sn(CN)_2$	537	82
$Sn(SCN)_2$	487	95
$Sn(ONC)_2$	506	93
$Si(CN)_4$	315	76
$Si(SCN)_4$	292	82
$Si(ONC)_4$	310	79
$Pb(CN)_2$	454	82
$Pb(SCN)_2$	346	88
$Pb(ONC)_2$	386	87
$Cd(CN)_2$	372	75
$Cd(SCN)_2$	315	79
$Cd(ONC)_2$	340	79
$Bi(CN)_3$	324	75
$Bi(SCN)_3$	286	86
$Bi(ONC)_3$	316	80
$In(CN)_3$	412	82
$In(SCN)_3$	375	89
$In(ONC)_3$	369	86
$Zn(CN)_2$	315	76
$Zn(SCN)_2$	285	83
$Zn(ONC)_2$	310	79
$Ga(CN)_3$	348	74
$Ga(SCN)_3$	302	79
$Ga(ONC)_3$	326	76
$Ge(CN)_4$	390	78
$Ge(SCN)_4$	352	86
$Ge(ONC)_4$	389	82
$Mg(CN)_2$	320	79
$Mg(SCN)_2$	289	89
$Mg(ONC)_2$	341	85

Table 29

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Ti(CN)_3$	265	75
$Ti(SCN)_3$	251	77
$Ti(ONC)_3$	263	75
$V(CN)_2$	275	81
$V(SCN)_2$	245	82
$V(ONC)_2$	263	80
$Mn(CN)_2$	278	82
$Mn(SCN)_2$	261	87
$Mn(ONC)_2$	275	85
$Sb(CN)_3$	315	76
$Sb(SCN)_3$	281	80
$Sb(ONC)_3$	298	78

Table 29-continued

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Cr(CN)_3$	301	82
$Cr(SCN)_3$	275	84
$Cr(ONC)_3$	280	83
$Fe(CN)_2$	269	75
$Fe(SCN)_2$	245	79
$Fe(ONC)_2$	257	79
$W(CN)_4$	215	81
$W(SCN)_4$	201	82
$W(ONC)_4$	210	81
$Co(CN)_2$	269	78
$Co(SCN)_2$	245	84
$Co(ONC)_2$	253	80
$Ni(CN)_2$	275	82
$Ni(SCN)_2$	257	86
$Ni(ONC)_2$	261	81
$Cu(CN)_2$	251	77
$Cu(SCN)_2$	235	80
$Cu(ONC)_2$	246	78
$Mo(CN)_3$	235	77
$Mo(SCN)_3$	211	79
$Mo(ONC)_3$	225	77
$Ca(CN)_2$	325	78
$Ca(SCN)_2$	314	84
$Ca(ONC)_2$	322	80
$Ba(CN)_2$	333	79
$Ba(SCN)_2$	301	87
$Ba(ONC)_2$	311	81
$Nb(CN)_2$	222	82
$Nb(SCN)_2$	201	83
$Nb(ONC)_2$	216	81
$Sr(SCN)_2$	314	84
$Sr(ONC)_2$	322	80

Table 30

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$ZnSn(CN)_4$	402	87

Table 30 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$MgSn(SCN)_4$	382	92
$CaSn(SCN)_4$	382	92
$Sr(SCN)_4$	382	92
$FeSn(ONC)_4$	376	91
$NiSn(CN)_4$	398	88
$CoSn(SCN)_4$	375	93
$MnSn(ONC)_4$	390	92
$TiSn(CN)_5$	385	87
$CuSn(SCN)_4$	360	93
$NiPb(CN)_4$	382	83
$CoPb(SCN)_4$	362	85
$MnPb(ONC)_4$	375	84
$ZnPb(CN)_4$	395	84
$MgPb(SCN)_4$	376	89
$CaPb(SCN)_4$	376	89
$SrPb(SCN)_4$	376	89
$FePb(ONC)_4$	375	89
$TiPb(CN)_5$	376	84
$CuPb(SCN)_4$	326	89
$CuIn(CN)_5$	355	84
$FeIn(SCN)_5$	335	91
$CoIn(ONC)_5$	345	88
$MgIn(CN)_5$	365	85
$CuBi(CN)_5$	324	78
$FeBi(SCN)_5$	315	87
$BaBi(ONC)_5$	320	83
$CaBi(CN)_3$	321	77
$MgBi(CN)_3$	315	78

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 8.

The batteries using the metal or semi-metal cyanide, cyanate, or thiocyanate of Example 8 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 9

The electrode characteristics of various metal and semi-metal tungstates specified in Table 31 and used as the anode active material were evaluated in Example 9.

Table 31 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 31

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_3(WO_4)_3$	292	86
$AlWO_4$	301	83
$SnWO_4$	477	94
$Sn_2W_3O_8$	436	95
$Sn(WO_4)_2$	402	96
$Si(WO_4)_2$	282	95
$PbWO_4$	405	95
$PbWO_3$	419	94
$CdWO_4$	326	91
$CdWO_3$	345	90
Bi_2WO_6	382	90
$Bi_2(WO_4)_3$	368	92
$In_2(WO_4)_3$	426	90
$In(WO_3)_3$	398	94
$Sb_2(WO_4)_3$	350	90
$ZnWO_4$	208	86
$ZnWO_3$	226	89
$Ga_2(WO_4)_3$	321	89
$Ga_2(WO_3)_3$	333	88
$Ge(WO_4)_2$	341	89
$Ge(WO_3)_2$	353	86
$MgWO_4$	301	87
$MgWO_3$	313	86
$CaWO_4$	301	87
$CaWO_3$	313	86
$SrWO_4$	301	87
$SrWO_3$	313	86

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 9.

The batteries using the metal or semi-metal tungstate of Example 9 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 10

The electrode characteristics of various metal and semi-metal molybdates specified in Table 32 and used as the anode active material were evaluated in Example 10.

Table 32 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 32

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(MoO_4)_3$	302	87
$SnMo_2O_8$	426	94
$SnMoO_4$	472	92
$SiMo_2O_8$	340	90
$PbMoO_4$	456	94
$CdMoO_4$	346	91
$Bi_2(MoO_4)_3$	402	93
$In_2(MoO_4)_3$	436	94
$InMo_4O_6$	398	96
$Sb_2(MoO_4)_3$	348	90
$ZnMoO_4$	268	87
$Ga_2(MoO_4)_3$	359	89
$GeMoO_4$	371	90
$MgMoO_4$	324	88
$CaMoO_4$	324	88
$SrMoO_4$	324	88

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 10.

The batteries using the metal or semi-metal molybdate of Example 10 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 11

The electrode characteristics of various metal and semi-metal titanates specified in Table 33 and used as the anode active material were evaluated in Example 11.

Table 33 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 33

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$AlTiO_5$	326	73
$SnTiO_4$	443	82
$SiTiO_8$	321	75
$PbTiO_3$	476	80
$PbTi_3O_7$	402	81
$CdTiO_3$	354	76
Bi_2TiO_5	498	81
$Bi_2Ti_2O_7$	424	82

Table 33 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
In_2TiO_5	478	83
$Sb_3Ti_2O_{10}$	369	80
$ZnTiO_3$	324	76
$GaTiO_5$	371	75
$GeTiO_3$	380	74
$MgTiO_4$	334	71
$CaTiO_4$	334	71
$SrTiO_4$	334	71

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 11.

The batteries using the metal or semi-metal titanate of Example 11 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 12

The electrode characteristics of various metal and semi-metal zirconates specified in Table 34 and used as the anode active material were evaluated in Example 12.

Table 34 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 34

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Al_2(ZrO_3)_3$	304	71
$SnZrO_3$	484	78
$SiZrO_4$	342	76
$PbZrO_3$	466	77
$CdZrO_3$	357	71
$Bi_2(ZrO_3)_3$	419	77
$In_2(ZrO_3)_3$	443	78
$Sb_2(ZrO_3)_3$	354	75
$ZnZrO_3$	294	73
$Ga_2(ZrO_3)_3$	372	74
$GeZrO_3$	379	72
$MgZrO_3$	339	73
$CaZrO_3$	339	73
$SrZrO_3$	339	73

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 12.

The batteries using the metal or semi-metal zirconate of Example 12 as the anode active material have the

improved cycle characteristics, compared with the prior art metal oxides.

Example 13

The electrode characteristics of various metal and semi-metal vanadates specified in Table 35 and used as the anode active material were evaluated in Example 13.

Table 35 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 35

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$AlVO_4$	319	82
SnV_2O_6	452	89
$Sn_2V_2O_6$	489	87
SiV_2O_7	324	84
$Pb_2V_2O_6$	477	86
PbV_2O_6	427	88
CdV_2O_6	326	83
$BiVO_4$	436	86
Bi_2VO_5	496	85
$InVO_4$	498	85
In_2VO_5	504	83
$SbVO_4$	354	83
ZnV_2O_6	311	81
$GaVO_4$	368	83
GeV_2O_6	341	84
MgV_2O_6	312	79
CaV_2O_6	312	79
SrV_2O_6	312	79

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 13.

The batteries using the metal or semi-metal vanadate of Example 13 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 14

The electrode characteristics of various metal and semi-metal chromates specified in Table 36 and used as the anode active material were evaluated in Example 14.

Table 36 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 36

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$AlCrO_3$	342	87
$SnCrO_4$	463	94
Sn_2CrO_6	504	92
$Si(CrO_4)_2$	341	89
Pb_3CrO_6	511	91
$PbCrO_4$	484	93
$CdCr_2O_4$	324	87
$BiCrO_3$	432	91
Bi_2CrO_6	426	93
$InCrO_3$	445	92
In_2CrO_6	486	90
$Sb_2(CrO_4)_3$	352	88
$ZnCrO_4$	336	87
$Ga_3(CrO_4)_2$	381	86
$GeCrO_4$	382	85
$MgCr_2O_7$	304	87
$CaCr_2O_7$	304	87
$SrCr_2O_7$	304	87

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 14.

The batteries using the metal or semi-metal chromate of Example 14 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 15

The electrode characteristics of various metal and semi-metal niobates specified in Table 37 and used as the anode active material were evaluated in Example 15.

Table 37 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 37

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$AlNbO_4$	324	71
$SnNb_2O_6$	424	75
$Sn_2Nb_2O_7$	468	74
$SiNbO_4$	342	71
$PbNb_2O_6$	403	74
$Pb_2Nb_2O_7$	426	72

Table 37 (continued)

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$Cd_2Nb_2O_7$	314	71
$BiNbO_4$	415	73
$InNbO_4$	445	74
$SbNbO_4$	370	73
$ZnNb_2O_6$	204	71
$GaNbO_4$	364	72
$GeNb_2O_6$	368	73
$MgNb_2O_6$	301	72
$CaNb_2O_6$	301	72
$SrNb_2O_6$	301	72

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 15.

The batteries using the metal or semi-metal niobate of Example 15 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 16

The electrode characteristics of various metal and semi-metal tantalates specified in Table 38 and used as the anode active material were evaluated in Example 16.

Table 38 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 38

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
$AlTaO_4$	302	81
$Sn_2Ta_2O_7$	476	88
$SiTa_2O_7$	272	82
$Pb_2Ta_2O_7$	406	87
$Cd_2Ta_2O_7$	314	84
$BiTaO_4$	404	86
$InTaO_4$	446	85
$SbTaO_4$	364	85
$Zn_2Ta_2O_7$	246	83
$GaTaO_4$	356	81
$Ge_2Ta_2O_7$	346	81
$Mg_2Ta_2O_7$	304	79
$Ca_2Ta_2O_7$	304	79
$Sr_2Ta_2O_7$	304	79

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No

deposit of metallic lithium was observed in any of the test cells of Example 16.

The batteries using the metal or semi-metal tantalate of Example 16 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Example 17

The electrode characteristics of various metal and semi-metal manganates specified in Table 39 and used as the anode active material were evaluated in Example 17.

Table 39 shows the discharge capacities of the test cells and the capacity maintenance rates of the cylindrical batteries at the 100-th cycle measured under the same conditions as those of Example 1.

Table 39

Salt	Discharge capacity (mAh/g)	Capacity maintenance rate(%)
Al_2MnO_6	326	80
$SnMnO_3$	486	89
$SnMn_2O_4$	424	90
$SiMnO_3$	314	81
$PbMnO_3$	443	87
$CdMnO_3$	369	82
Bi_2MnO_4	424	84
Bi_2MnO_6	412	86
In_2MnO_4	461	84
In_2MnO_6	452	84
Sb_2MnO_4	392	83
Sb_2MnO_6	376	84
$ZnMnO_3$	314	81
Ga_2MnO_4	386	81
$GeMnO_3$	349	82
$MgMnO_3$	326	78
$CaMnO_3$	326	78
$SrMnO_3$	326	78

After the conclusion of cathode polarization of the test cells in the tenth cycle, the test cells were decomposed. No deposit of metallic lithium was observed in any of the test cells of Example 17.

The batteries using the metal or semi-metal manganate of Example 17 as the anode active material have the improved cycle characteristics, compared with the prior art metal oxides.

Although all the above examples refer to the cylindrical batteries, the principle of the present invention is not restricted to this structure but may be applicable to secondary batteries of various types, such asd coin-type, rectangular-type, and cylinder-type.

In the above examples, $LiMn_{1.8}Co_{0.2}O_4$ was used as the cathode active material. The similar effects can be exerted for a variety of other cathode active materials allowing reversible charge and discharge operations, such as $LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$, and the like.

As discussed above, the present invention uses an anode of high capacity and excellent cycle life and thereby provides a non-aqueous electrolyte secondary battery that is free of a short circuit due to dendrite and has a higher energy density and a high reliability.

Claims

1. A non-aqueous electrolyte secondary battery comprising a cathode capable of being charged and discharged, a non-aqueous electrolyte, and an anode capable of being charged and discharged, said anode having an active material that comprises a salt of a metal or a semi-metal and a compound selected from the group consisting of oxo-acids, thiocyanic acid, cyanogen, and cyanic acid, wherein each said oxo-acid comprises an element selected from the group consisting of nitrogen, sulfur, carbon, boron, phosphorus, selenium, tellurium, tungsten, molybdenum, titanium, chromium, zirconium, niobium, tantalum, manganese, and vanadium, salts of said oxo-acids of phosphorus and boron being restricted to hydrogenphosphates and hydrogenborates.

2. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said anode comprises a mixture of said active material, carbon material, and a binding agent.

3. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal or semi-metal is at least one selected from the group consisting of Al, Sn, Si, Pb, Cd, Bi, In, Zn, Mg, Ge, Ga, Ca, Ba, Sr, B, Ir, Sb, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Nb.

4. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of nitrogen is at least one selected from the group consisting of nitrates and nitrites.

5. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of sulfur is at least one selected from the group consisting of sulfates, sulfites, disulfates, peroxomonosulfates, peroxodisulfates, thiosulfates, dithionates, disulfites, thiosulfites, dithionites, and sulfoxylates.

6. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of phosphorus is at least one selected from the group consisting of monohydrogenphosphates, dihydrogenphosphates, phosphinates, and phosphonates.

7. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of boron is at least one selected from the group consisting of monohydrogenborates and dihydrogenborates.

8. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of selenium is at least one selected from the group consisting of selenates $M_2(SeO_4)_m$, selenites $M_2(SeO_3)_m$, $M_2(SeO_5)_m$, $M(HSeO_4)_m$, and $M(HSeO_3)_m$, where M denotes a metal or semi-metal having a valence m.

9. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said metal salt or semi-metal salt of said oxo-acid of tellurium is at least one selected from the group consisting of $M_6(TeO_6)_m$, $M_2(TeO_4)_m$, $M_5(H_5TeO_6)_m$, $M_4(H_2TeO_6)_m$, $M_2(H_3TeO_6)_m$, and $M_2(H_4TeO_6)_m$, where M denotes a metal or semi-metal having a valence m.2

FIG. 1

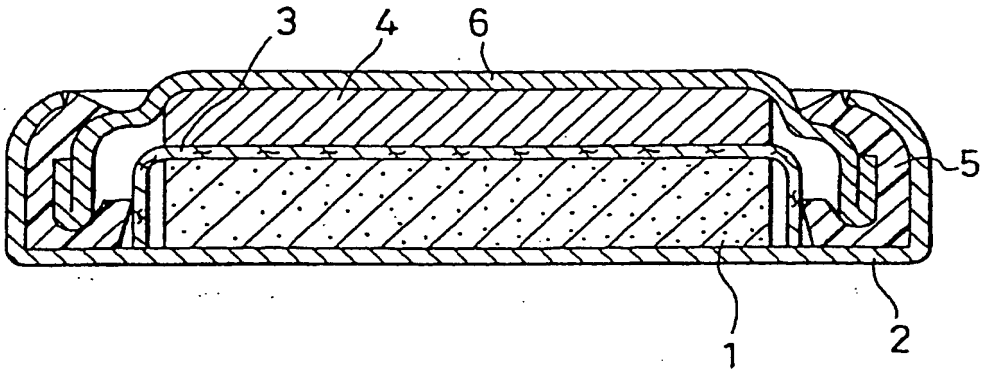
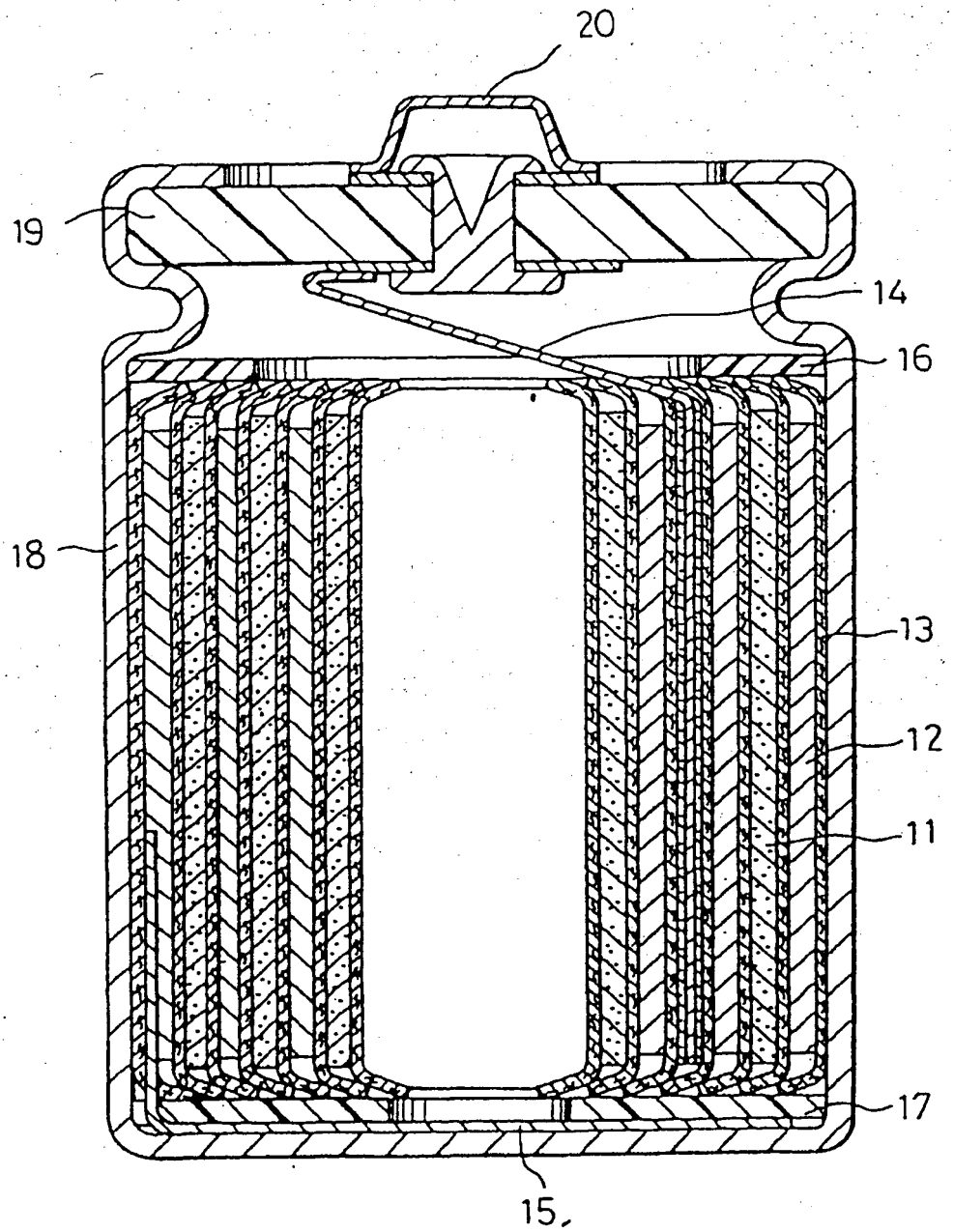


FIG. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 97 12 2297

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 626 (E-1636), 29 November 1994 & JP 06 243870 A (SANYO ELECTRIC CO LTD), 2 September 1994, * abstract *	1,4,5	H01M4/62 H01M4/48 H01M4/58
X	US 5 474 861 A (BITO YASUHIKO ET AL) * claims 1-17 *	1,2	
A	EP 0 413 331 A (RAY O VAC CORP) * claims 1-20 *	1-9	
A	EP 0 582 410 A (SANYO ELECTRIC CO) * claims 1-14 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 April 1998	Battistig, M

CATEGORY OF CITED DOCUMENTS

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